

## Development of carbon nanomaterials through chemical routes

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**Abstract** Development and characterization of nanophase materials is the new research thrusts, world-wide, in advanced materials. Among various nano-materials developed in the last decade, carbon nanomaterials (nanofibers and tubes) have attained maximum attraction of the researchers all as industries. This is mainly because of the extraordinary properties of carbon nanotubes (CNTs) resembling metal, semiconductor as well as superconductor and also for their hydrogen storage capacity. Carbon nanotubes have been synthesized by numerous techniques, such as arc discharge, laser ablation, catalytic CVD etc.

With the attractive properties of carbon nanotubes and the potential applications in mind, there has been concerted efforts world-wide to produce these materials in more economical way. In our laboratory, we have launched programs to synthesize aligned carbon nanomaterials through chemical methods. Aligned carbon nanomaterials have been synthesized through CVD method by cracking of hydrocarbon gases (benzene, xylene etc.) in presence of catalyst (Fe, Ni etc.) at temperature of 700–800°C. The substrate was prepared through sol-gel route in order to control the size and distribution of catalyst particles. Benzene leads to development of more carbon nanofibers while higher concentration of nanotubes are observed with xylene as precursor. The relative amounts of aligned and randomly oriented carbon nanotubes can be controlled through optimized processing conditions. Nanotubes have also been synthesized using solids (chars and cokes). The precursors are impregnated with a suitable catalyst solution. On heating these precursors to a temperature of 650–900°C, carbon nanotubes have been observed embedded in amorphous carbons. These carbon nanomaterials have been characterized using XRD, TEM, SEM and thermal analysis techniques.

**Keywords** Carbon nanomaterials, synthesis and characterization, CVD, XRD, TEM, SEM

**PACS Nos.** 61.46.+w, 61.10.Nz, 68.37.Hk, 68.37.Lp

### 1. Introduction

The urge for making the devices smaller, more efficient and versatile has opened a new era of Nanoscience world comprising nanoscience, nanomaterials and nanotechnology. Nanomaterials and technology represent a new class of materials and devices with unique properties and potential for applications to address important needs of human beings [1,2]. A central aspect of nanoscience world is the development of nanomaterials, of size below 100 nm. In addition to quite different properties and performance, these materials are made in a fundamentally different way, embedded as atom by atom or atomic layer by layer. As a result, a vast new field of research has emerged dealing with the fabrication of various types of nanomaterials, their devices, properties, performance and understanding basic scientific aspects explaining these [3,4]. To date carbon has in various forms, contributed to the welfare of human being, may it be as electrodes and electronic components, adsorbants for environmental protection or high strength carbon fibers and

composites for structural applications. This is greatly due to the diverse structural forms and functions of carbons. Carbon, in fact, has played an important role in the origin of nanoscience world with the discovery of fullerenes followed by carbon nanotubes. Today carbon nanomaterials exist in various forms, as layered materials, nano clusters, fullerenes, nanofibers and nanotubes. Among these carbon nanotubes (CNTs) have been attracting much attention because of their unique physical properties and potential for large industrial applications. These materials find wider applications as sensors, energy storage, electrodes for lithium ion batteries as well as in microelectronic and communication devices. Carbon nanotubes are thought to have remarkable mechanical properties with theoretical Young's modulus calculated as around 5.5 TPa and theoretical strength as 200 GPa. These high values make these ideal as reinforcement in new generation composites. However, this requires large scale production of carbon nanotubes in less expensive and easier way. The CNTs have generally been synthesized by arc-discharge, laser evaporation and chemical deposition methods [5–7]. Amongst these, catalytic chemical vapour deposition

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method promises to be simple, more controllable and suitable for large-scale production. The properties of the end product depend on chirality, diameter, linearity and purity, which in turn controlled by the fabrication method [8].

In our Institute studies have been undertaken to develop different types of carbon nanomaterials using catalytic vapour deposition techniques as well as *in situ* formation of carbon nanotubes in the solid carbons during their pyrolysis.

The present paper reports on development of carbon nanomaterials over quartz and silica-nickel oxide based substrates (SNS) using benzene and xylene as carbon source and ferrocene as a catalyst.

## 2. Experimental

### 2.1. Description of the CVD apparatus :

The experimental apparatus used for the preparation of the carbon nanomaterials is schematically shown in Figure 1. The reactor is made of 550 mm long quartz tube of 35 mm inner diameter placed in a tubular electrical furnace. The substrate, which is the site of the nanomaterials formation, was placed in pyrolysis zone of the horizontal quartz reactor. The temperature control in the pyrolysis zone was carried out using programmable temperature controller.

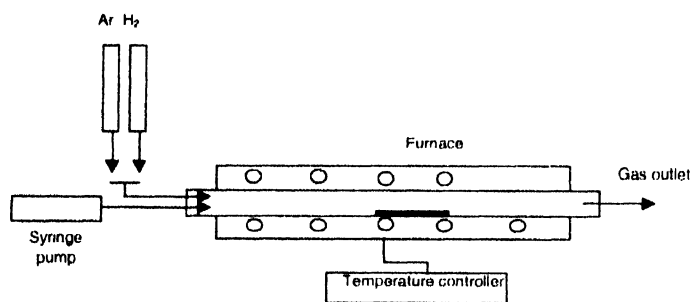


Figure 1. Experimental set up used for the synthesis of carbon nanotubes

### 2.2. Materials used :

Benzene and xylene were used as gaseous precursors while chemically modified polymeric materials were used as solid precursors. Ferrocene and nickel were used as catalyst. High purity E. Merck grade chemicals were used for the present studies.

### 2.3. Preparation of silica-nickel substrate (SNS) by sol-gel route :

In order to have uniform distribution of nickel particles in the substrate, these were prepared in the Institute using sol-gel method. Nickel nitrate solution was mixed into 1 : 4 : 2 mole ratio of TEOS : water : ethanol respectively. In the hydrolyzed system, the ratio of nickel nitrate to TEOS was varied between 0.01–0.03. The mixture of nickel nitrate and TEOS system was stirred

continuously for 12 hrs on magnetic stirrer at room temperature. The mixture was casted at room temperature for gelation. The gels obtained were kept in an oven at 60°C for aging and drying. The dried gels were further post cured to 250°C temperature. The post-cured flat casts were used as silica-nickel oxide based substrates (SNS).

### 2.4. Synthesis of carbon nanomaterials :

The experimental set up shown in Figure 1 was first flushed with argon. For development of carbon nanofibers, benzene vapour, along with a suitable catalyst were inserted into the hot zone along with argon. The temperature was maintained at 800–900°C.

For development of carbon nanotubes, hydrogen gas was passed into the system at 550°C for reduction of the substrate. Subsequently, the temperature in the pyrolysis zone was raised to 700°C–800°C. On attainment of the temperature, the gas mixture of argon, hydrogen gas was introduced into the horizontal quartz reactor at appropriate flow rate. The hydrocarbon source (xylene) containing about 1 wt.% of catalyst was injected in the reactor by the syringe pump. In hydrocarbon solution, xylene is a carbon source and ferrocene act as a catalyst for the nanotube formation. The injection feed rate was varied with the series of experiments and also with the reaction time and temperatures. After the reaction, the furnace was allowed to cool under argon atmosphere. All substrates, used in these studies, were weighed before and after the reaction to determine the amount of carbon produced at different sites within the reactor.

### 2.5. Characterization of carbon nanomaterials :

The characterization of product was carried out by Scanning Electron Microscope (SEM) Hitachi S-3000N, Transmission Electron Microscope (TEM) Philips, Tecnai-20 model. XRD analysis of the nanomaterials was carried out by X-Ray Diffractometer Philips, X'pert model. TGA of carbon materials was carried out on Mettler Thermal Analysis system TA 4000 with TG50 for getting information about amount of catalyst present in the product and also for oxidation behaviour of carbon nanotubes.

## 3. Results and discussion

The process of formation of carbon nanomaterials consists of cracking of hydrocarbon source into carbon and carbon rich species, consolidation of these and growth. All these, though temperature dependent processes, are accelerated with the presence of catalyst. The growth shape is controlled by the size of the floating catalyst particles as well as by the growth compounds such as base catalyst. In the present case the iron was used as floating catalyst and nickel as base catalyst. Further, the source also leads to different types of carbon nanomaterials. Benzene and xylene are preferred to give carbon nanomaterials of different architectures.

### 1. Development of carbon nanofibers from benzene :

Figures 2(a) and (b) show the SEM images of carbon nanomaterials produced from benzene and SNS. These exhibit the growth of vapour grown nanocarbon fibers (VGNCFs) on

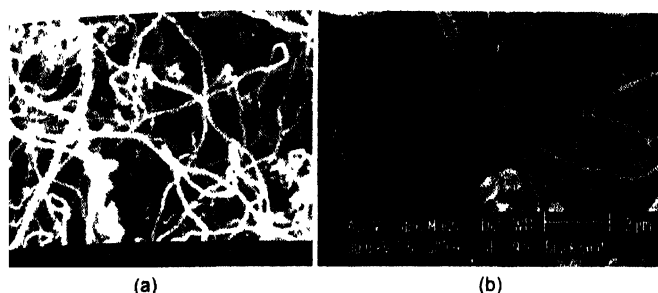


Figure 2(a, b). SEM micrographs of carbon nanomaterials from benzene (growth in random manner on SNS)

SNS surface. The diameter varies from 100 to 500 nm and about more than 80  $\mu\text{m}$  in length. Figure 3 shows TEM micrograph of these VGNCFs. It shows well-aligned graphitic planes. Small amount of catalyst can also be seen near the ends of the fibers. XRD pattern of these fibers is shown in Figure 4. It shows peak at  $2\theta = 26.5$  corresponding to graphite. However, the peak is not sharp due to turbostratic nature of the layers.



Figure 3. TEM micrograph of VGNCFs

### 2. Development of carbon nanotubes from xylene :

Carbon nanotubes were developed from mixture of xylene and ferrocene at temperature of 700–800°C. The ferrocene-xylene

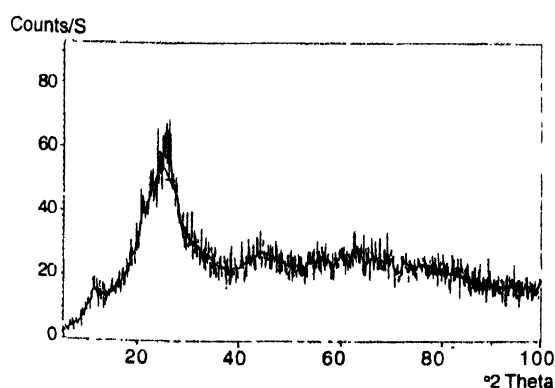


Figure 4. XRD pattern of VGNCFs.

solution which contains both catalyst and carbon source supplied with the help of carrier gas decomposed at elevated temperature. The ferrocene (catalyst) is helpful for the formation of nanotube form of carbon on different substrates surface. In case of silica-nickel oxide based substrate, nickel performs secondary role of catalyst for the formation of CNTs. Bimetallic complex of iron and nickel gave better results in terms of growth and alignment as compared to other substrates. From this solution (mixture), high density with close contact carbon nanotubes were grown. As such, Van der Waals interaction between the tubes keeps them growing in a well-aligned manner and of high density.

The CNTs arrays were grown on different substrates for a total time of 30 min and 60 min. The carbon nanotubes in the arrays are very clean with uniform diameter of about 25–65 nm. Since the reactor is made up of quartz tube, its inner walls can also act as growth sites for aligned CNT arrays. The growth direction of carbon nanotubes was towards the axial center of the tube. This aligned nanotube arrays deposited on quartz can easily be peeled off from the quartz surface without destroying the arrays integrity. Figure 5 shows the relation between carbon deposition yield and injection feed rate of solution containing

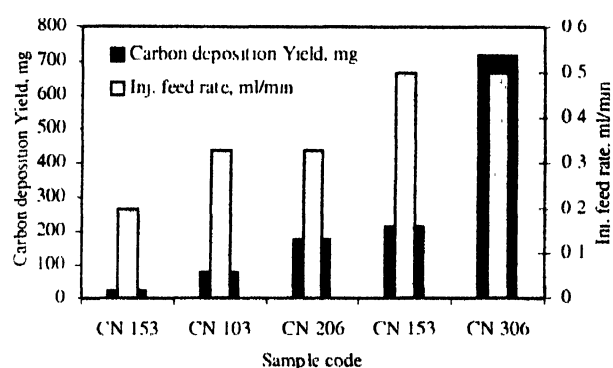


Figure 5. Relation between carbon deposition yield with injection feed rate.

ferrocene and xylene. It reveals that 0.5 ml/min injection feed rate in CN 306 gives better yield of about 720 mg as compared to other experiments. The higher feed rate of solution provides abundant Fe particles and carbon source. The continuous

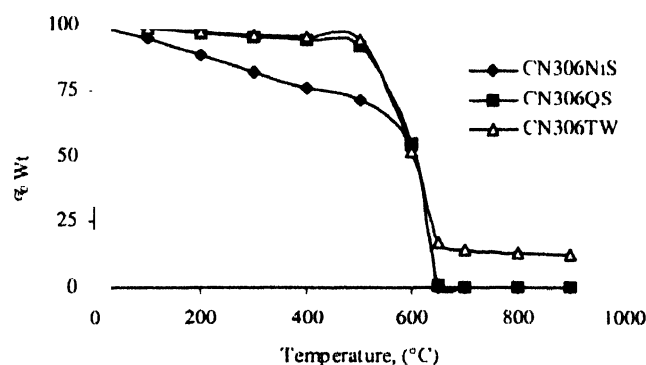
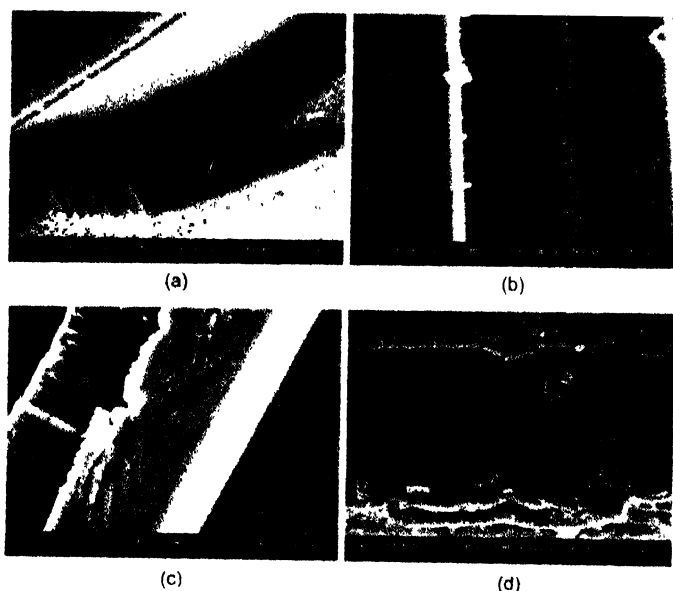


Figure 6. TGA graph of CNTs deposited on different substrates

feeding method secures the continuous supply of Fe catalyst particles and carbon source during the continuous growth process of aligned carbon nanotubes. These trapped particles may maintain a rapid continuous growth of carbon nanotubes. So, higher feed rate gives better results and provides higher growth rate of carbon nanotubes. The feed rate not only enhances the yield but also size of the nanotubes. This is evident from table Figure 6 shows the TGA graphs of CNTs produced on different substrate site. It gives information about presence of catalyst on different sites and oxidation behaviour of CNTs. The percentage wt. loss at relevant temperature indicates that CNTs oxidize at about 600–700°C and also that by optimizing the process parameters, carbon nanotubes can be made with no trapped catalyst as indicated by complete weight loss on oxidation.

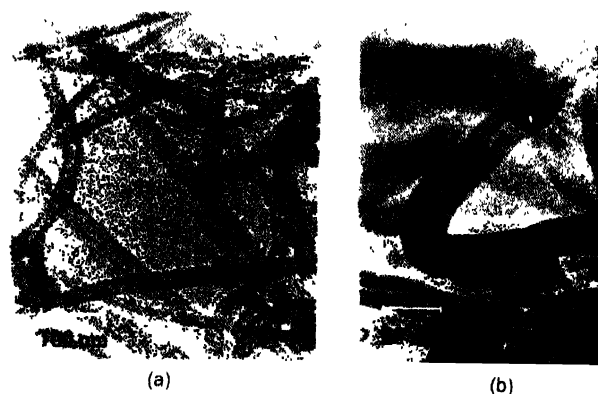
Figure 7a shows CNT arrays grown on the surface of silica-nickel oxide based substrate (SNS). This layer of CNTs has well-defined morphology and all of the tubes are almost of the same height around 65  $\mu\text{m}$ . This image presents features of CNTs with densely packed and vertically aligned growth mechanism on the surface of substrate. Figure 7b shows same nature of



**Figure 7.** SEM micrographs of (a) CNTs aligned in vertically on the silica-nickel oxide based substrate (SNS), (b) CNTs aligned in horizontally on SNS, (c) growth of CNTs upper and lower side of the SNS and (d) CNTs vertically grown on substrate with more than 500  $\mu\text{m}$  length.

aligned CNTs but it is in horizontally aligned manner with respect to substrate and are of length more than 100  $\mu\text{m}$ . Figure 7c shows growth of aligned CNTs on upper and lower surface of SNS. Figure 7d is SEM image of as-grown CNTs film on the surface of silica-nickel oxide based substrate with a growth time of 60 minutes. The length of the carbon nanotubes is more than 500  $\mu\text{m}$ , so the average growth rate calculated is about 8  $\mu\text{m}/\text{min}$ . Figure 8a shows TEM image of CNTs produced from ferrocene-xylene mixture on substrate surface. No encapsulation of catalyst

is observed in cavity of these CNTs. Figure 8b shows TEM micrograph bent carbon nanotube. It reveals the flexibility of carbon nanotubes.



**Figure 8(a, b).** TEM image of CNTs produced from ferrocene-xylene mixture.

Work is in progress to get higher growth rate by improving other reaction conditions.

#### 4. Conclusions

The catalytic decomposition of xylene and benzene on different substrates leads to formation of vapour grown nanocarbon fibers and carbon nanotubes. Bimetallic complex catalyst system shows enhanced growth of these nanomaterials. Studies on different substrates revealed that carbon deposition depends on the substrate type. The silica-nickel oxide based substrate shows better results as compared to quartz substrate. The yield and purity of CNTs can be increased by further optimization of experimental conditions. The injection CVD method provides the basis for synthesis of aligned CNTs with vertical or horizontal fashion growth on suitable substrate. The increase in carbon deposition and aligned growth of CNTs will open new avenues for potential applications. The CVD method is a simple and efficient method to develop carbon nanomaterials with desired configurations.

#### Acknowledgments

TEM observations were made at Sophisticated Instrumental Centre for Advance Research and Testing (SICART), Vall Vidyanagar. The authors are thankful to SICART and Mr. G. Patel for rendering help in these observations.

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